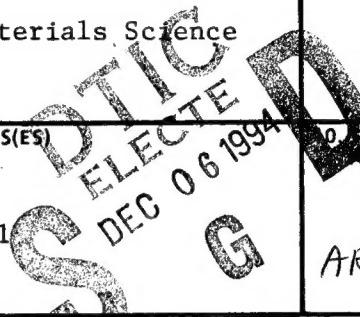


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<p>13. ABSTRACT (Maximum 200 words)</p> <p style="text-align: right;">DTIC QUALITY INSPECTED 6</p> <p>In carrying out research on aluminum-glasses (<math>\text{Al}</math>-glasses), several unusual results are found:      (i) Submillimeter ductile glassy ribbons are obtained. (ii) Significant enhancement in the tensile strength is measured in <math>\text{Al}</math>-glass ribbons with <math>\text{Al}</math> nanocrystallites embedded in them. (iii) Deformation induced crystallization within the shear bands is observed for the first time. (iv) Strong <math>\text{Al}</math>-transition metal interaction is inferred from x-ray and neutron diffraction measurements. These results have added to our understanding of formation and microstructure-mechanical effect relationships of metal-glasses, and also to the technological values of these materials. We have begun to apply our findings to the synthesis and studies of bulk metallic-glass and nanocrystalline alloys. Thus far, we have succeeded in making subcentimeter glasses based on rare-earths and magnesium-tin, nanocrystalline alloys based on refractory metals via conventional casting, and as well as, centimeter <math>\text{Al}</math>-glass button via consolidation of amorphous powders obtained by ball-milling. In collaboration with Professor T. Egami at U. Penn., a method for obtaining two-dimensional atomic pair distribution is developed to unravel the structure of decagonal crystals. The new method will be applied to study layered materials.</p>			
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## Synthesis and Structural Properties of New Metallic Phases Exhibiting Non-Crystallographic Symmetries

### Statement of the problem studied:

The objectives of our research are to synthesize new aluminum-based metallic glasses and quasicrystalline alloys, to investigate their atomic-scale structures, and to study their thermal stability and formation in order to shed light on the unusual formability of the new materials. Structures of the new materials are studied by x-ray, electron, and neutron diffraction, including that of high-resolution diffraction. The structure-property relationships in systems of technological importance are also being investigated.

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### Summary of the most important results:

#### (1) Unfolding the atomic-scale structure of decagonal crystal -

In collaboration with Professor T. Egami (U. Penn), a technique for carrying out 2-dimensional structural analysis in layered structure is developed. Pair distribution function (PDF) in 2-d is obtained for the first time. The x-ray measurement was carried out on decagonal crystal of AlCuCo with a positive sensitive detector (PSD) placed perpendicular to the diffraction plane. With the PSD, we were able to collect the Bragg intensities from the sub-layers of the quasiperiodic planes. The results are found to agree well with a structural model for the decagonal crystal based on aggregation of clusters proposed by S. Burkov. This finding establishes the atomistic structure of a 2-d quasicrystal. Perhaps even more important is that the technique developed will provide a very powerful tool for investigating 2-d disordered systems.

#### (2) Investigation of criteria for glass formation -

In an effort to understand the unusual vitrification of Al-alloys that can form submillimeter ribbons and Mg-alloys that can form millimeter rods, several ternary and quaternary systems have been mapped with respect to glass formability. The latter is measured by the maximum thickness of

amorphous ribbons obtainable by single-roller melt spinning. For the Al-alloys, typical compositions are Al-TM1-TM2-RE, where TM=transition metal, RE=rare earth including Y; the Mg-alloys are Mg-(Cu,Ni)-X where X is Zn and other polyvalent elements. Thus, the chemistry of the alloys studied involves three types of atomic characters. Clearly, strong hybridization of s and d orbitals is prominent between them. It is found that glass formability is optimized in the Al-Fe-Ni-Gd and Mg-Cu-Sn systems. Our study has provided the first test for our conjecture that strong and competing atomic interactions brought about by the diverse types of elements can lead to "confusions" in the atomic order, thus favoring vitrification. In comparison, previous criteria for good glass formation are more empirical, mainly they revolve around the mismatch in atomic size. It is inferred that improvement in the vitrifiability of high-strength and good corrosion resistance light-metal glasses leading to samples of larger dimensions can be expected in systems that involve more than three atomic characters.

### **(3) Synthesis of bulk metallic glasses by conventional casting -**

We have developed a casting technique for making bulk samples directly from the melt. There is a preliminary success in obtaining bulk metallic glasses of some magnesium-based alloys. Samples are in the form of 2 mm-diameter rods. We have begun to explore the formation of bulk glasses in the rare-earth and refractory-metal based systems. To carry out the search, we employ the electronic-factor principle mentioned above as our guide. Bulk Nd-Al-TM metallic-glass rods with diameters up to 6 mm have been produced. We have also obtained a homogeneous mixture of nanocrystals embedded in a glassy matrix in both Cu- and Ni-based 4-mm rods. It is expected that in both these systems the glassy state can be obtained upon composition variation. Meanwhile, it is note-worthy that nanocrystalline alloys, whose recrystallization temperatures may exceed the crystallization temperatures of glasses, are important from the technology standpoint. Our systematic approach for forming bulk metallic glasses and nanocrystals is clearly working and many more bulk-sample forming systems can be expected in the future.

**(4) Consolidation of amorphous powders obtained by mechanical alloying -**

We have succeeded in amorphizing aluminum alloys by mechanical alloying. Amorphous  $Al_{80}Ni_8Fe_4Gd_8$  quaternary powders are produced using the mechanical alloying (MA) technique, suggesting that powder metallurgy may be applied to the manufacture of aluminum metallic glasses as high strength, low density engineering materials. Detailed investigations into the microstructural evolution of the amorphous phase from elemental powders have been completed employing scanning and transmission electron microscopy as well as other analytical techniques. The results support previous observations of the amorphization reaction by interdiffusion developed from studies of simple binary alloy systems. The resulting amorphous powder demonstrates good thermal stability, and consolidated amorphous bulks up to 93% dense are easily produced. The final products are found to have mechanical properties resembling ceramics of the brittle type.

**(5) Microstructure-mechanical property relationships -**

We have been carrying out fundamental studies of new metallic glasses, on both their structure and microstructural effect on mechanical properties. Such studies are important because they can shed light on the origin of easy vitrification and superior mechanical properties. The latter refers to our earlier observation of significant enhancement in the tensile strength of  $Al$ -glass matrix with  $Al$  nanocrystallites embedded in it. Our result can be contrasted with the embrittlement of some metallic glasses when they are annealed. It has long been speculated that embrittlement results from some kind of structural change, which has not been confirmed. We have observed, for the first time, deformation-induced crystallization within the shear bands of some  $Al$ -glasses. F.c.c.- $Al$  nanocrystallites are found exclusively within the shear band extending across the deformed ribbons. The nanocrystals can be produced by either bending or ball-milling. We conjecture that the deformation-induced structural change is due to local atomic rearrangements within the shear bands which exhibit enormous plastic strain. Furthermore, we find that the extent of atomic rearrangement depends on the short range order and chemical bonding strength of the amorphous state. From a technological viewpoint, this provides a means of forming nanocrystals where the formation of a product includes extrusion and some other type of deforming step.

**Publications Resulting From ARO Contract No. DAAL03-91-G-0009**  
(only refereed articles are listed).

1. Y. He, H. Chen, X.F. Meng, S.J. Poon, and G.J. Shiflet, "Stability investigation of a decagonal Al-Cu-Co quasicrystal", *Phil. Mag. Lett.* **63**, 211 (1991).
2. H. Chen, Y. He, G.J. Shiflet, and S.J. Poon, "Mechanical properties of partially crystallized aluminum based metallic glasses", *Scripta Metall.* **25**, 1421 (1991).
3. Y. He, H. Chen, S.J. Poon, and G.J. Shiflet, "The effect of temperature on stability of the Al-Cu-Co decagonal phase", *Phil. Mag. Lett.* **64**, 307 (1991).
4. H.Y. Hsieh, T. Egami, Y. He, S.J. Poon, and G.J. Shiflet, "Short range ordering in amorphous Al<sub>90</sub>Fe<sub>x</sub>Ce<sub>10-x</sub>", *J. Non-Cryst. Solids* **135**, 248 (1991).
5. Y. He, G.M. Dougherty, G.J. Shiflet, and S.J. Poon, "Unique metallic glass formability and ultra-high tensile strength in Al-Ni-Fe-Gd alloys", *Acta Metall. Mater.* **41**, 337 (1993).
6. Y. He, X. Yan, T. Egami, S.J. Poon, and G.J. Shiflet, "Synchrotron x-ray studies of diffuse scattering in an Al-Cu-Co 2D decagonal quasicrystal", *Phil. Mag. Lett.* **66**, 241 (1992).
7. Y. He, R. Hu, X. Yan, T. Egami, S.J. Poon, and G.J. Shiflet, "Two dimensional pair distribution functions from synchrotron x-ray data: application to an AlCuCo decagonal quasicrystal", *Phys. Rev. Lett.* **70**, 2411 (1993).
8. A.N. Mansour, S.J. Poon, Y. He, and G.J. Shiflet, "Native oxide chemistry of amorphous Al<sub>90</sub>Fe<sub>7</sub>Ce<sub>3</sub> alloy by angle resolved XPS", *J. Surf. Sci. Spectra*, **2**, 31 (1993).
9. G.M. Dougherty, G.J. Shiflet, and S.J. Poon, "Synthesis and microstructural evolution of Al-Ni-Fe-Gd metallic glass by mechanical alloying", *Act. Metall. Mater.* **42**, 2275 (1994).
10. H. Chen, Y. He, G.J. Shiflet, and S.J. Poon, "Bending induced nanocrystal formation in shear bands of aluminum-glasses", *Nature*, **367**, 541 (1994).
11. S.Y. Su, Y. He, S.J. Poon, and G.J. Shiflet, "Formation of Mg-based glasses and their mechanical properties", to be published in *Metall. Trans.*
12. Y. He, H. Chen, G.J. Shiflet, and S.J. Poon, "Studies of nucleation and growth in the crystallization of aluminum-glasses", in preparation.
13. Y. He, G.J. Shiflet, and S.J. Poon, "Mechanically induced deformation modes of aluminum-glasses", accepted for publication in *Acta Metall. Mater.*
14. G.M. Dougherty, Y. He, G.J. Shiflet, and S.J. Poon, "Compositional dependence of glass formability in Al-Fe-Ni-Gd Alloys", *Scripta Metall. et Mater.* **30**, 101 (1994).
15. S.J. Poon, Y. He, G.J. Shiflet, and G.M. Dougherty, "Synthesis and Properties of Bulk Amorphous and Nanocrystalline Alloys", to be published in Conference Proceedings from NATO Conference on Science and Technology of Rapid Solidification and Processing.

16. G.J. Shiflet, Y. He, S.J. Poon, G.M. Dougherty, and H. Chen, "Aluminum-Rich Metallic Glasses", to be published in Conference Proceedings from NATO Conference on Science and Technology of Rapid Solidification and Processing.
17. Y. He, G.J. Shiflet, and S.J. Poon, "Formation and Properties of Light-Metal Amorphous Alloys", to be published in Proceedings of ARO Sagamore 40th Materials Research Conference.

### **Participating Scientific Personnel**

**S. Joseph Poon - Principal Investigator**

**Gary J. Shiflet - Principal Investigator**

**H. Chen - Ph.D. awarded, 1992**

**Y. He - Ph.D. awarded, 1992**

**G.M. Dougherty - M.S. awarded, 1993**

**S.Y. Su - Graduate student (1992-1993)**

**B. Kolo - Graduate student (Ph.D.)**

**C. Price - Undergraduate (part-time)**